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**Non-Noble Catalysts and Catalyst Supports
For Phosphoric Acid Fuel Cells**

2nd Quarterly Report

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Introduction

Under this contract, work is being carried out on three tasks:

- I. Anode catalysts resistant to CO poisoning
- II. Cathode supports for Pt catalysts
- III. W-Ti carbide catalysts.

Under Task I, work has been principally directed toward the possibility that by supporting highly active, CO sensitive Pt upon weakly active, CO tolerant WC, an anode catalyst with intermediate activity and CO tolerance might be achieved. This possibility was suggested by observation by Bockris and McHardy [1] of enhanced specific activity of cathodic reduction of O_2 supported on sodium tungsten bronze, and by the likelihood [Hamilton, 2] that Pt will segregate to the WC surface, perhaps forming monolayer or sub-monolayer coverage. Evidence that very highly dispersed Pt can be prepared on WC was presented in our Oct. '79-July '80 progress report [3]. Pertinent results of this work were, (a) the Pt/WC dispersions appear to contain both a very highly dispersed and a more coarsely dispersed fraction of Pt, (b) H_2 oxidation polarization curves of thin, porous electrodes of these dispersions did not saturate at high overpotential as they would have if all the Pt contained were in microcrystals of the size inferred from proton stripping and plating measurements, and (c) the residual activity of one electrode studied in 2.9% CO/ H_2 saturated acid showed a total exchange current approximately equal to that which would result from the supporting WC alone, but a higher transfer coefficient, $\alpha = .52$ compared to .32 for the WC. In connection

with the objectives of this task, it is of interest to note that the $W_{1-x}Ti_xC$ cubic alloys currently under study in Task III display apparently complete tolerance to poisoning by 2.9% CO included in the H_2 gas feed in measurements made in 1M H_3PO_4 at 23 C.

Task II was motivated by our past observation [4] of exceptional stability of several refractory hard metals, notably TaN and TaB, at high overpotential in H_3PO_4 . These offer the possibility of corrosion free performance as O_2 reduction catalyst supports in acid fuel cells.

In Task III, H_2 oxidation studies on the cubic alloy system $Ti_{1-x}W_xC_{1-y}$ were undertaken to clarify the nature of the active sites on tungsten-carbon catalysts. Specific points of interest are the effects of the cubic structure (WC is hexagonal), the variation of the activity with W content (TiC alone is active), and the effect of the deviation of the bulk C concentration from stoichiometry.

Work During the Reporting Period

TASK I - As noted in the introduction, the data so far obtained for Pt dispersed on WC suggest that Pt is present in two forms: as microcrystalline Pt and a surface dispersion of Pt-W-C. Some uncovered WC may also be present. Thus far, we have not yet been successful in producing Pt/WC dispersions free of microcrystalline Pt, and thus unable to directly determine the properties of the hypothesized surface Pt-W-C dispersion. Although we are continuing our effort to produce such dispersions, we are now attempting to assess the validity of the simple three catalyst picture by computer modelling of

the available data. Polarization data in 2.9 CO/H₂ saturated acid [3] suggest that the Pt-W-C catalyst follows simple Tafel kinetics with transfer coefficient $\alpha = 0.5$. WC shows Tafel kinetics with $\alpha = 0.3$ [5]. The kinetic relation for Pt has been derived by Vogel et al. [6]. The loss in activity for Pt in the presence of CO is attributed to simple site blockage [6]. Assuming the same to hold true for the Pt-W-C surface dispersion, and further assuming that all three catalysts are uniformly distributed through the thin porous electrodes, it is readily shown that the H₂ oxidation current is

$$I(V) = (2FQADc_0x) \tanh(Lx)$$

where

$$x = (W_1 E^2 F + W_2 G + W_3 H)^{1/2}$$

$$E = [\theta_0 + (1 - \theta_0) \exp(FV/RT)]^{-1}$$

$$F = \exp(2FV/RT)$$

$$G = \exp(\alpha_2 FV/RT)$$

$$H = \exp(\alpha_3 FV/RT)$$

$$W_i = (f_i \gamma_i i_0^i) / 2FDc_0 \text{ with } i = 1 \text{ for Pt, 2 for}$$

WC,

and 3 for Pt-W-C.

Here I is electrode H₂ oxidation current,

V - overpotential, F the Faraday constant, Q - electrode roughness factor,

A - electrode cross section area, L - electrode thickness,

D - the H₂ diffusion coefficient, c_0 - the H₂ saturation concentration, θ_0 - the equilibrium hydrogen coverage on Pt,

R the gas constant, T - the absolute temperature, α the

transfer coefficient, i_0 exchange current density, γ - catalyst surface areal density and $0 \leq f \leq 1$ the catalyst poisoning factor .

We have also assumed the hydrogen reaction equilibrium potential to be the same on all catalysts, and proton diffusion to be much faster than H_2 molecule diffusion.

Starting values of α_0 , f , and i_0 for Pt in 1M H_3PO_4 at 23°C have been obtained by fitting H_2 oxidation data on Pt sheet. For WC, α , i_0 , and $f \approx 1$ are known. For Pt-W-C, α and i_0 are deduced from polarization curves obtained with 3% CO/ H_2 and f is a disposable parameter.

At the least, these computations should confirm or disprove the simple picture suggested by the trends in the experimental data, and quantitative characterization of the Pt-W-C surface dispersion is a viable possibility .

The observed behavior of our Pt/WC dispersions in CO, suggestive of the presence of a Pt-W-C surface dispersion displaying simple Tafel kinetics, with i_0 approximately equal to that of the host WC ($i_0 = 0.6 \times 10^{-7} \text{ A/cm}^2$) but with higher transfer coefficient, .52 vs .32 for the WC, makes preparation and study of Pt on WC of higher activity very desirable. Two commercial preparations of WC expected to have high activity were tested. Both had very high BET areas, but the exchange current densities were quite low. An in-house preparation of WC with $i_0 = .3 \times 10^{-6} \text{ A/cm}^2$, a factor of ~ 5 higher than that used up to the present time, is available and will be employed for this purpose.

TASK II - Chloroplatinic acid has been precipitated on TaN (BET area = 0.22 m₂/gm), at a loading of 1 mgm of Pt per gm of TaN, or 0.4 μgm of Pt per cm₂ of TaN, a value suggested by our earlier experience with Pt on WC [3].

TASK III - During this reporting period, work was continued on the cubic Ti_{1-x}W_xC_{1-y} alloys. Values of x and y for the 4 samples studied are listed in Table 1, together with BET areas, exchange current densities for H₂ oxidation, and transfer coefficients for H₂ oxidation and evolution. In addition, one alloy has been carefully studied in 2.9% CO/H₂ saturated 1M H₃PO₄ at 23°C, and another in H₂ saturated 85 w/o H₃PO₄ at 54, 70, and 84°C in an effort to determine the activation energy.

Logarithmic plots of the H₂ oxidation current (taken as the difference between observed currents in H₂ and N₂ saturated acid) vs. overpotential in 1M H₃PO₄ are shown in Figs. 1 to 4. These data were analyzed via the current-voltage relation of thin porous electrode model with Tafel kinetics [7],

$$I(V) = QA(2 FDC_0 i_{OY} \exp [FV/RT])^{1/2} \\ \times \text{TANH} (L [i_{OY}/2FDC_c]^{1/2} \exp [\alpha FV/2RT])$$

where the symbols are defined under TASK I.

The limiting cases

$$I(V) = QA(2FDC_0 i_{OY})^{1/2} \exp [\alpha FV/2RT] \text{ for } V \gg \infty$$

$$I(V) = QAL_Y i_{OY} \exp [\alpha FV/RT] \text{ for } V \gg 0, \text{ and the relation}$$

$$L(i_{OY}/2FDC_0)^{1/2} = \exp [-\alpha FV_c/2RT]$$

which holds at the potential V_c of the intersection of the high and low V limiting cases are useful diagnostic tools.

The observed transfer coefficients appear to be valid. Given the geometry of the electrodes and the low observed current densities, there is no reason to believe mixed control occurs at low V . But for the samples with $x = .44$ and $.47$, the values of i_0 calculated from observations and known electrode parameters are very low, and a mixed control region is observed, but not expected, for H_2 oxidation. (See Figs. 3 and 4.) For the $x = .23$ and $.31$ samples, only the reaction controlled region is expected, and only the reaction controlled region is observed.

Apparently, the $x = .44$ and $.47$ powders are not completely wetted. This problem became evident when preparing electrodes of the $x = .47$ sample, which is quite fine. When attempting to study this sample in 85 w/o H_3PO_4 , the problem was severe; only weak wetting occurred, evidenced by slight H_2 evolution. Evidence for non-wetting for the $x=.44$ sample is less direct. The powder is coarse (grain size $38\mu m$, but BET area of $2.3 m^2/gm$), and surface tension effects are not perceptible. Strongest evidence for non-wetting of these samples is the presence of the mixed control region of the characteristic curves. As is evident from the equations above, when the characteristic curve shows both reaction and mixed control regions, internal checks, yielding effective estimates of the geometric characteristics of the electrodes, can be obtained. The $x = .23$ and $.31$ electrodes we take to be completely wetted (though this may not be completely true). We then obtain effective values of the cross-sectional area and thickness for the $x = .44$ and $.47$ electrodes, and from them estimate i_0 , listed as i_0^{CORR} in TABLE 1.

All of the samples have been cursorily checked for CO tolerance in 1M H_3PO_4 at 23°C. The $x = .47$ sample was more carefully checked. In the overpotential range $0.03 \leq V \leq .16$ volts (RHE), $\Delta V = .01$ volts, with 2.9% CO/H_2 and H_2 feeds, the mean fractional difference in H_2 oxidation current between the CO contaminated and pure feed curves was -2.5%. This lies within the reproducibility of the measurements, but strongly indicates that in these compounds, as in WC and $\text{Mo}_{1-x}\text{W}_x\text{C}$, CO is neither oxidized nor acts as a poison, but rather, simply dilutes the H_2 feed. These data were obtained on one of the incompletely wetted samples. But at no time was there any indication during the long point by point scans of any increase in activity which would be expected from increased wetted area.

The polarization studies at elevated temperature in 85 w/o H_3PO_4 were carried out on the $x = .44$ sample which also appears to be incompletely wetted. Two problems arose here. We cannot at the moment rule out progressive wetting. We went from low temperature to high, and did not recheck at low temperature. However, no change was observed during any of the repetitive runs. In addition to this uncertainty, a progressive shift in the polarization curves with temperature was observed. Checking the apparatus via voltammetric sweeps on a Pt sheet electrode, using for reference the mean positions of the two strong H adsorption-desorption extrema, we observed substantial temperature dependent shifts attributable to variation in the potential of the dynamic reference electrode.

These shifts can be completely eliminated with appropriate changes in the reference electrode current. Moreover, the magnitude of the shifts in the high temperature carbide data can be estimated. (Not all the shift is necessarily attributable to this source.) Appropriate values of temperature dependent shifts in reference potential were then applied to the high temperature $x = .44$ data, and a rough estimate made of the activation energy. For the $x = .44$ sample, at 0.04 volts, in the activation controlled region, $E_a = 7 \pm 2$ kcal/mol, and at 0.24 volts in the mixed control region, $E_a = 3 \pm 1$ kcal/mol. (The value of 12 kcal/mol given in the January monthly narrative was made before the reference shift data were obtained.) These are, of course, very rough estimates, and better controlled measurements will be made.

The poor wetting at higher W concentrations, and the possibility of incomplete wetting at lower concentrations, introduce an unacceptable uncertainty in the measurements, and we are presently seeking an alternative electrolyte which will wet these carbides and permit confident comparison of the exchange current density with variations in x , y , and combinations thereof. Again, we believe the transfer coefficients to be reliable.

Despite the uncertainties in the present data, and granted the validity of the transfer coefficients, the lack of sensitivity to CO, and the similarity of E_a to that of WC, we conclude that H_2 oxidation proceeds on $Ti_{1-x}W_xC_{1-y}$ as on WC and $Mo_{1-x}W_xC$, with proton discharge as the rate determining step [5].

It becomes interesting then, to compare the activity of WC_{1-y} with that of $Ti_{1-x}W_xC_{1-y}$. This is done, on the basis of presently available data, in Fig. 5. Note that we are now focusing attention on the effect of carbon deficiency in WC_{1-y} . The WC_{1-y} data displayed were taken from the work of Ross and Stonehart [8] who provided not only measured activities on a number of differently prepared samples, but total carbon content and Auger analyses of these samples as well. From the compositional data, two estimates of the carbon deficiency can be made, assuming the W-sublattice to be full (behavior characteristic of the transition metal monocarbides). The horizontal width of the WC_{1-y} blocks in Fig. 5 reflects the difference in these estimates. The measured activities at 0.05V were adjusted to 54°C using $E_a = 9000$ cal/mol, the value we obtained for near zero overpotential [5]. An uncertainty of 10% was assumed for the measured currents.

For the $Ti_{1-x}W_xC_{1-y}$ alloys, some adjustment must be made for the non-unity W exchange. If the assumed reaction mechanism is valid and no strong surface segregation occurs, the activity of these alloys is expected to vary at least as x^2 . Comparison of i_0^{CORR} with y , powers of x , and the product of y with powers of x supports this expectation. The spread of y values for the Ti alloys in Fig. 5 were obtained from chemical analyses, and from reported values [9] of the $\delta + C$ two phase boundary at 1500°C. (All but one sample showed unreacted carbon.) Only one sample, $x = .31$, shows notable

deviation from the phase diagram data. Uncertainties in i_0^{CORR} for $\text{Ti}_{1-x}\text{W}_x\text{C}_{1-y}$ result from those of fitting the characteristic curves, BET area, and electrode geometry, and in the cases of $x = .44$ and $.47$, from the propagation of these uncertainties in estimating effective values of the geometrical constants of the electrodes. Adjustment to 54°C in concentrated acid was made by scaling data for all 4 samples by the factor observed for the $x = .44$ sample. Also, a factor accounting for the different surface cell densities of the alloys was used.

Despite the large uncertainties in the data displayed in Fig. 5, a definite dependence on bulk carbon deficiency is indicated, with no distinction discernible between the activity dependence of the cubic and hexagonal carbides on bulk carbon deficiency. Taken together these data suggest that the active sites on a W-C H_2 oxidation catalyst consist of 2 or more W near neighbors of a C surface defect.

Planned Work

TASK I - We will pursue the computer modelling work described, and prepare dispersions of Pt on higher activity WC.

TASK II - Reduction of the Pt precipitation and H and O stripping measurements will be carried out to characterize the TaN dispersion.

TASK III - The most important job here is to find a suitable, wetting electrolyte to enable direct observation of the variation of i_0 with x and y . This accomplished, the $x = .23$ sample should serve to normalize the results with respect to H_3PO_4 and permit reliable comparison with other carbide data obtained in that acid.

TABLE 1

| x | y | BET AREA m ² /gm | α_{ox} | α_{ev} | i_o 10 ⁻⁸ A/cm ² | i_o^{CORR} 10 ⁻⁸ A/cm ² |
|-----------|-----------|--------------------------------|---------------|---------------|---|--|
| .23 ± .01 | .03 ± .01 | .8 | .21 ± .01 | .57 | (.6 ± .2) | .6 ± .2 |
| .31 ± .01 | .06 ± .03 | 1.3 | .15 ± .01 | .36 | (.8 ± .2) | .8 ± .2 |
| .44 ± .02 | .06 ± .01 | 2.3 | .14 ± .01 | .59 | .17 ± .05 | 5 ± 3 |
| .47 ± .02 | .9 ± .01 | 1.6 | .28 ± .02 | .39 | (.4 ± .1) | ± 7 |

Properties of cubic $Ti_{1-x}W_xC_{1-y}$

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Figure Captions

1. H_2 oxidation current vs overpotential (RHE) in 1M H_2PO_4 at 23°C, for $Ti_{.77}W_{.23}C_{.97}$. Linear fits yielding data of Table 1 shown.
2. As Fig. 1, except $Ti_{.69}W_{.31}C_{.94}$.
3. As Fig. 1, except $Ti_{.56}W_{.44}C_{.94}$.
4. As Fig. 1, except $Ti_{.53}W_{.47}C_{.96}$.
5. Specific current density at 0.05V, 54°C, in concentrated H_3PO_4 , vs y: shaded, WC_{1-y} ; open, $Ti_{1-x}W_xC_{1-y}$. For the Ti alloy, current has been divided by x^2 . Other adjustments to data discussed in text.

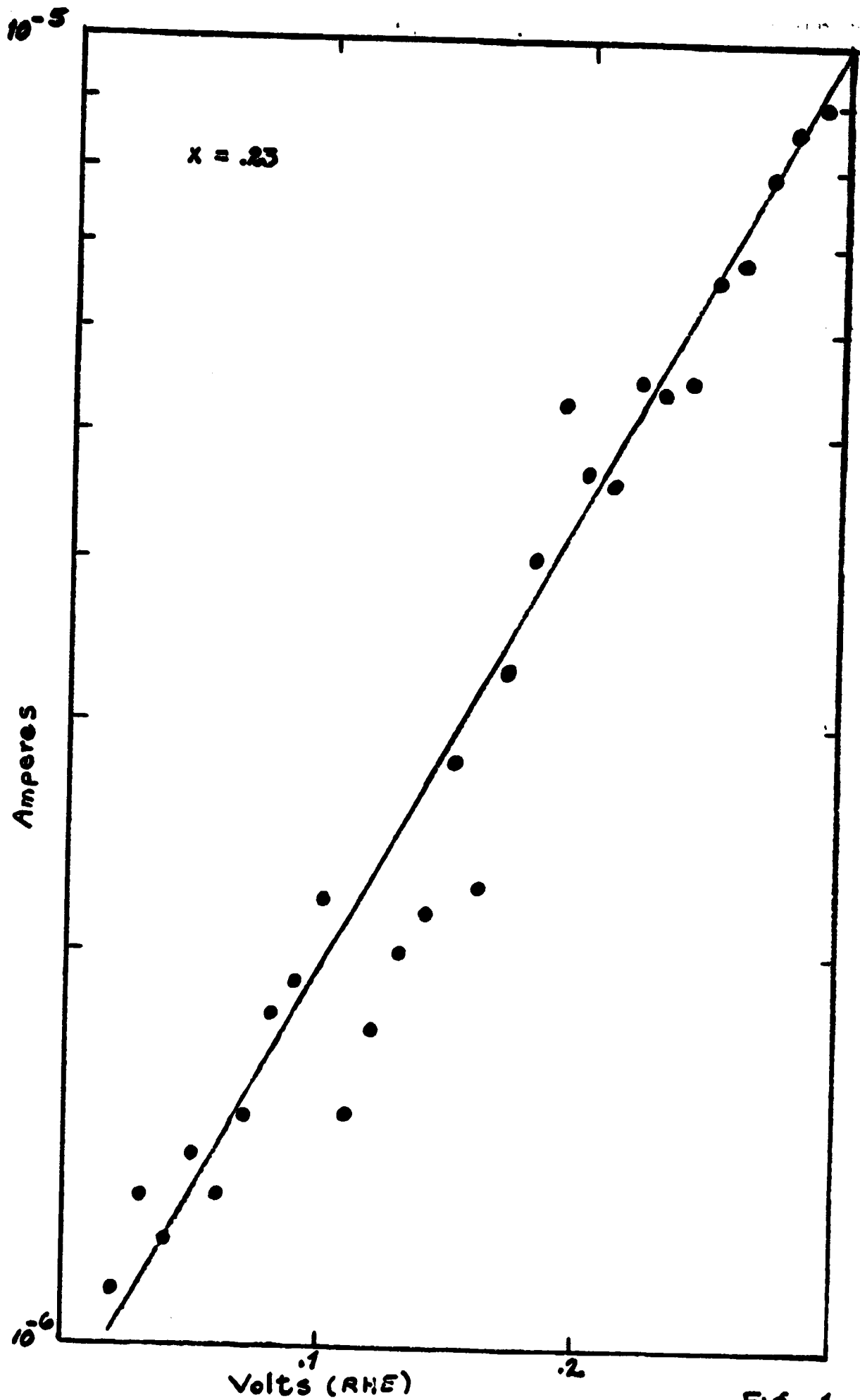


Fig. 1

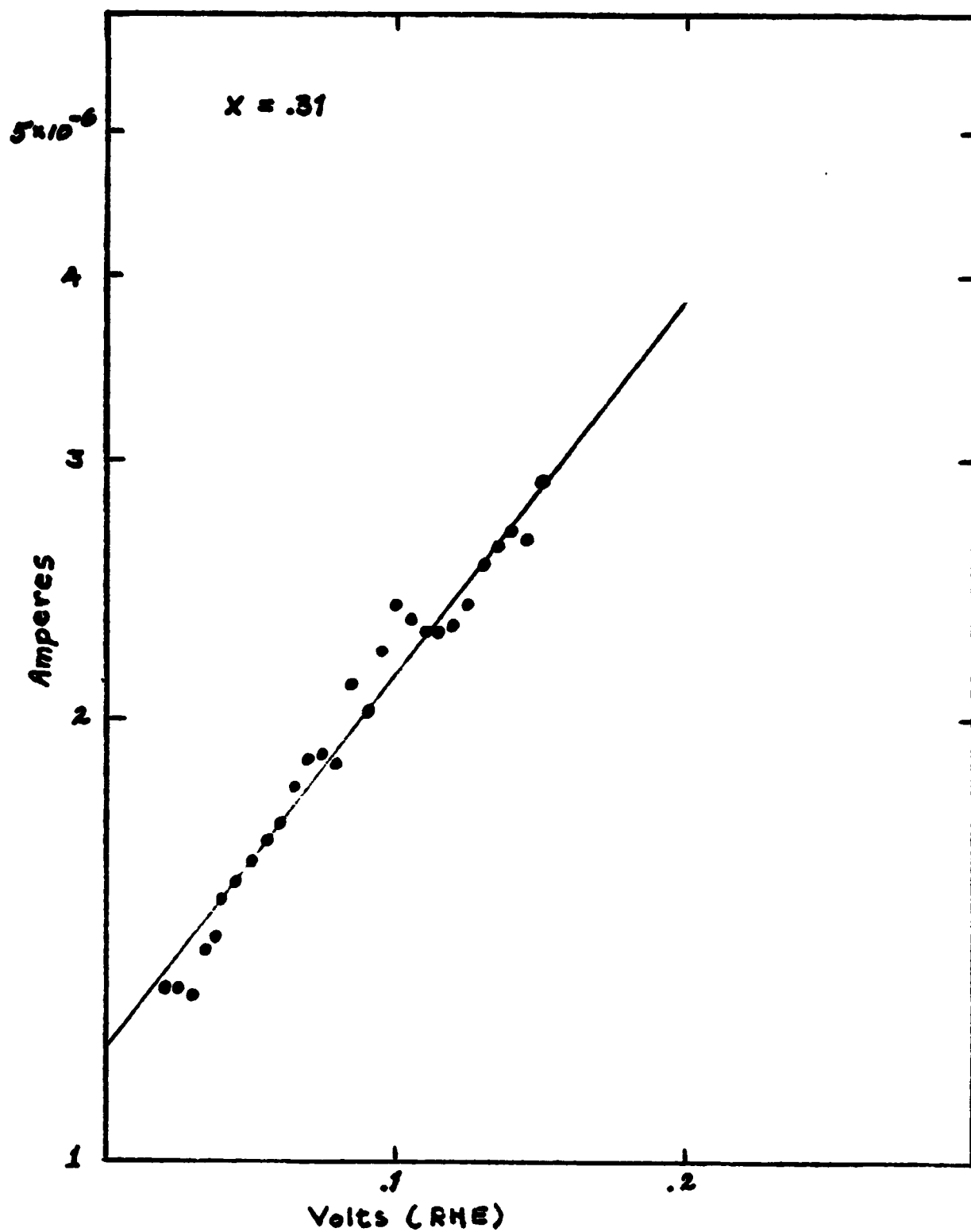


Fig. 2

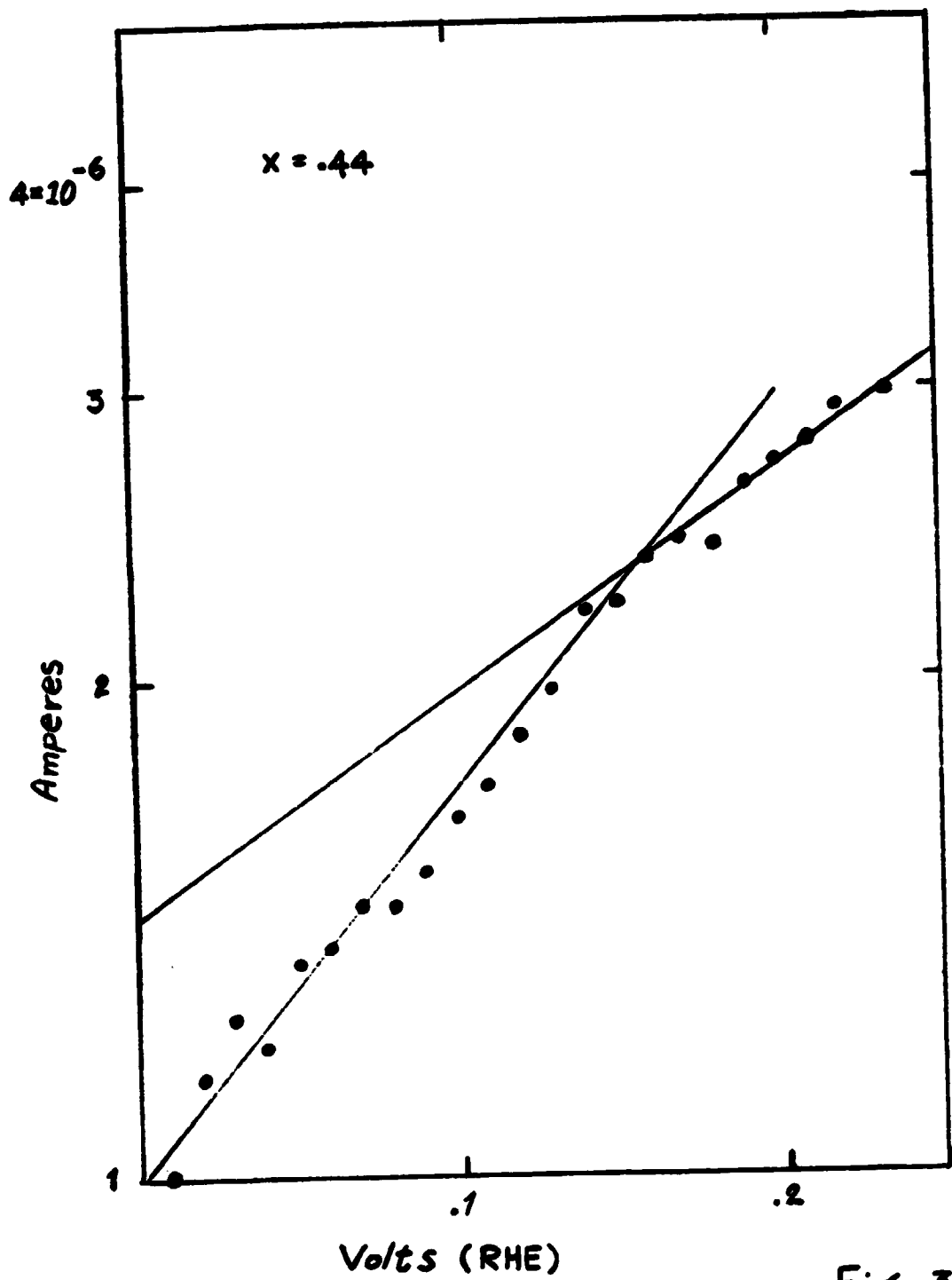


Fig. 3

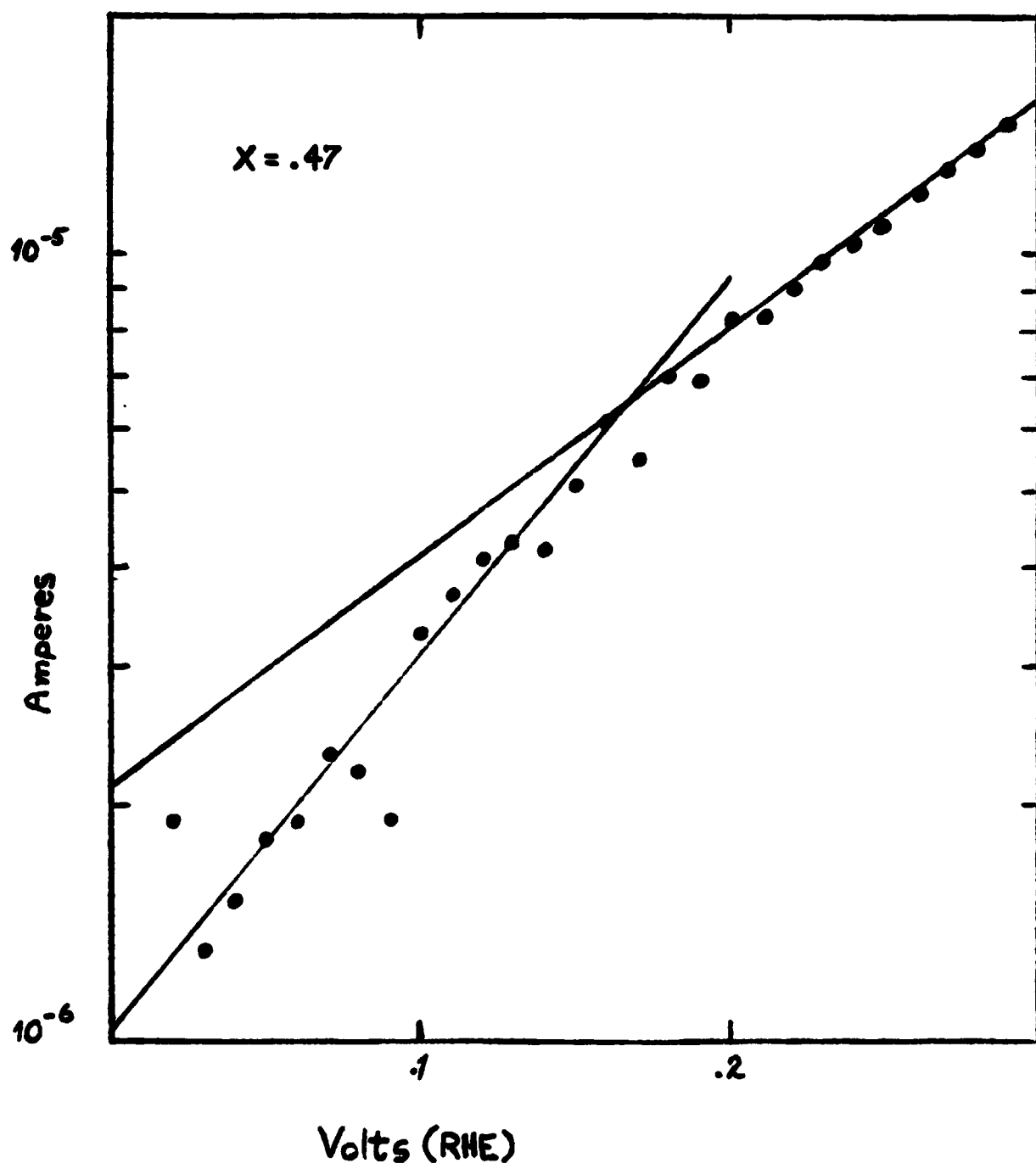


Fig. 4

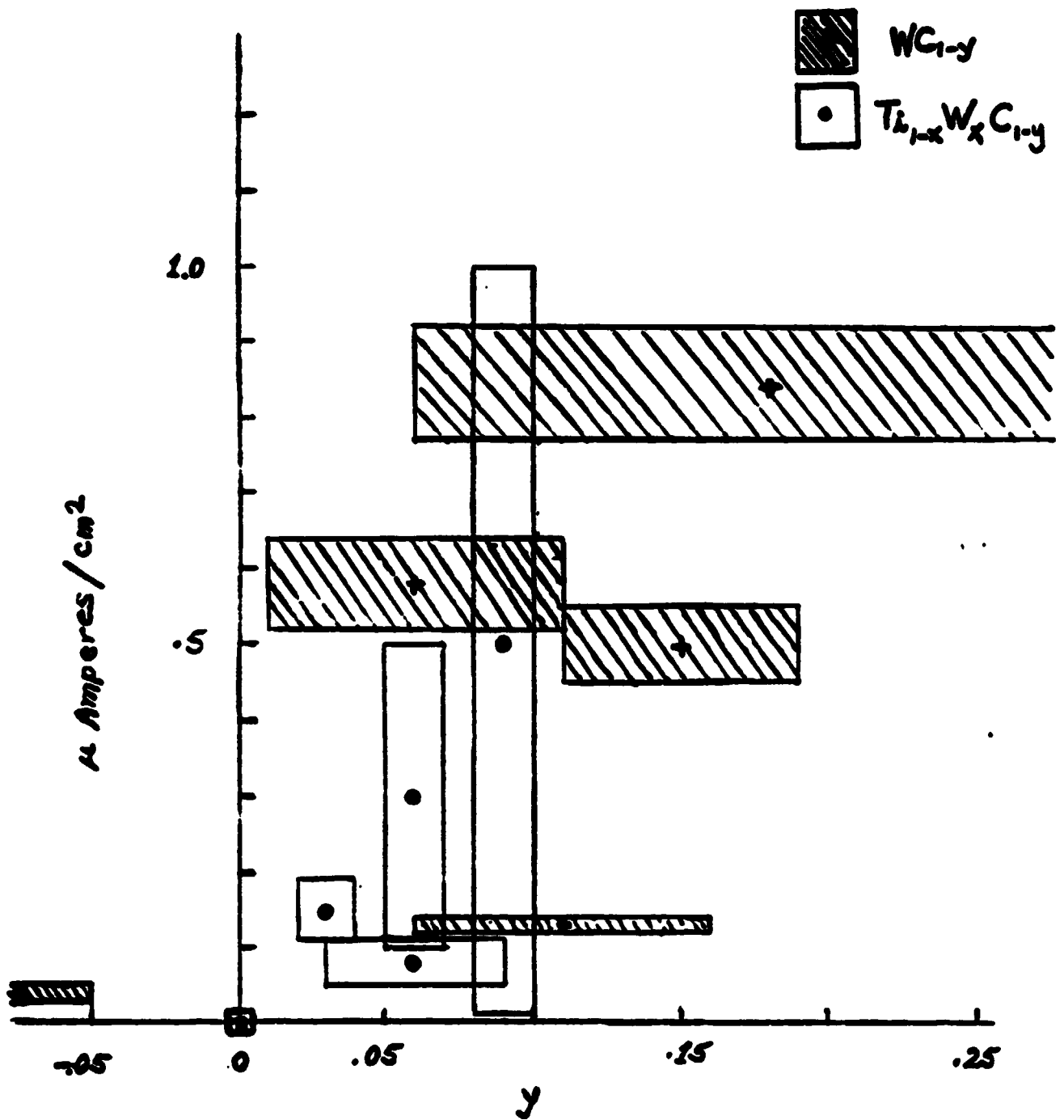


Fig. 5

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